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This project examined the fundamental processes of surface reactions using infrared spectroscopy. The novelty of this project was the development of a dynamic infrared spectroscopic technique capable of following reaction dynamics on well defined single crystal surfaces. The dynamic infrared technique was applied to two experiments. The first experiment was used to follow single shot experiments: the technique was used to follow thermally induced reactions using temperature programmed reflection absorption infrared spectroscopy (TPRAIS). The second experiment is to follow dynamics of repetitive processes combining modulated molecular beams with reflection infrared. This has been demonstrated for simple adsorption-desorption of CO on Pt; difficulties in achieving proper conditions for film growth have precluded the application to film deposition, but we are continuing to pursue this problem.

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8. Publications:

"Characterization of Pt electrodes by Infrared Spectroscopy", J. B. Benziger, F. A. Pascal, S. L. Bernasek, M. P. Soriaga and A. T. Hubbard, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 198, 65-80 (1986).

"The Isosteric Phase Transformation of the Ni(100)-c(5√2 x 5√2) R45° CO Surface", J. B. Benziger and G. R. Schoofs, Surface Science 171, L401-408 (1986).

"Considerations in Building a Low Noise Reflection Absorption Infrared Spectrometer", J. B. Benziger, R. E. Preston and G. R. Schoofs, Applied Optics 26, 343-354 (1987).

"Adsorbate Induced Reconstruction of p(2x2)X Adlayers on Ni(100)", J. B. Benziger, G. R. Schoofs and A. K. Myers, Langmuir 4, 268-276 (1988).

"Effect of Methyl Substitution on the Interaction of Benzene with Ni(100): An Experimental and Theoretical Study", A. K. Myers and J. B. Benziger, Langmuir 3, 343-354 (1987).

"Comparison of Benzene Adsorption on Ni(100) and Ni(111)", A. K. Myers, G. R. Schoof and J. B. Benziger, Journal of Physical Chemistry 91, 2230-2232 (1987).

"Reactions of Organonitrogen Compounds on Ni(100)", G. R. Schoofs and J. B. Benziger, Journal of Physical Chemistry 92, 741-749 (1988).

"Reaction Thermodynamics of Hydrocarbons with Ni(100)", G. R. Schoofs and J. B. Benziger, Langmuir 4, 526-532 (1988).

"Reaction Dynamics of Acetate Decomposition by Temperature Programmed Reflection Infrared Spectroscopy", J. B. Benziger and E. W. Scharpf, Journal of Physical Chemistry 91, 5531-5534 (1987).

"Reactions of Pyrrole with Ni(100)", G. R. Schoofs and J. B. Benziger, Surface Science 192, 373-382 (1987).

"Aromatic Polymerization on Metal Surfaces", J. B. Benziger, N. Franchina and G. R. Schoofs, in Molecular Phenomena at Electrode Surfaces, M. P. Soriaga ed., American Chemical Society, Washington, DC, pp. 83-98 (1988).

"The Effect of Substituted Groups on the Interaction of Benzene with Ni(111)", A. K. Myers and J. B. Benziger, Langmuir, in press.

9.   Abstract of Objectives and Accomplishments

This project examined the fundamental processes of surface reactions using infrared spectroscopy. The novelty of this project was the development of a dynamic infrared spectroscopic technique capable of following reaction dynamics on well defined single crystal surfaces. The dynamic infrared technique was applied to two experiments. The first experiment was used to follow single shot experiments; the technique was used to follow thermally induced reactions using temperature programmed reflection absorption infrared spectroscopy (TPRAIS). The second experiment is to follow dynamics of repetitive processes combining modulated molecular beams with reflection infrared. This has been demonstrated for simple adsorption-desorption of CO on Pt; difficulties in achieving proper conditions for film growth have precluded the application to film deposition, but we are continuing to pursue this problem.

FINAL REPORT

SUBMITTED TO

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

SURFACE INTERMEDIATES IN

THIN FILM DEPOSITION

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Time Period: November 15,1986 - November 14,1988

AFOSR Grant No. 86-0050

INTRODUCTION

This project has been examining surface reactions in an effort to characterize the reaction intermediates and chemistry in thin film deposition. Dynamic infrared spectroscopy has been developed to follow transient events in a monolayer film on a well defined single crystal surface. Reaction intermediates during desorption and decomposition of organic species have been followed during temperature programming. Direct surface kinetics have also been determined with the use of modulated molecular beam scattering off surfaces. In a diversion from the original scope of the project we have developed variations on semiempirical molecular orbital calculations to describe adsorbed speices on surfaces using a large cluster (> 20 atoms) to define the surface. The molecular orbital calculations were found to be very illuminating in accounting for trends in adsorption and reactivity of substituted aromatic molecules on different crystal faces of nickel. An initial goal of the proposed work, to examine surface intermediates during silicon film deposition, has been hampered by contaminated molecular beam sources and inadequate beam fluxes to achieve adequate growth rates to measure with the experimental apparatus. This work is being continued and recent modifications to the experimental system appear to have promise for success.

THE INTERACTION OF AROMATIC MOLECULES WITH NICKEL

Aromatic molecules are known to undergo electrophilic substitution reactions, and the rate of substitution can be accelerated or decelerated due to the presence of substituent groups on the ring. Electrophiles attack the aromatic ring at locations of high electron density resulting in a carbonium ion complex intermediate. The elimination of a proton restores the aromatic character to the end product of reaction.

Metal surfaces can also facilitate electrophilic substitution reactions in aromatic molecules. The surface acts as an electron acceptor in similar fashion to an electrophile, and hence facilitate substitution reactions. The rate and directionality of the electrophilic substitution reactions on metal surfaces are affected by substituent groups according to the electron affinity of the substituent group. Electrophilic reactions on metal surfaces can produce some unique reactions, including surface polymerization of oriented aromatic polymers. This section discusses the nature of electrophilic interactions of benzene and substituted benzenes with nickel surfaces, and the surface polymerization of aromatic molecules on Ni surfaces.

The interaction of benzene and substituted benzenes with well defined nickel single crystal surfaces has been studied with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), temperature programmed reaction (TPR), and reflection absorption infrared spectroscopy (RAIS). The apparatus and experimental techniques have been described

in detail elsewhere [1].

To help interpret the experimental results the adsorption of the molecules with the surfaces of interested was modelled with a modified extended huckel theory (EHT) that included electron-electron and nuclear repulsions [2]. These calculations were helpful in understanding the nature of the adsorption bonds and the reactivity of the adsorbed molecules.

Effect of Surface Structure on the Adsorption of Benzene

The adsorption of benzene on Ni surfaces was found to be very sensitive to the crystal orientation whereas the decomposition of benzene was found to be insensitive to crystal orientation and thermodynamically controlled. The TPR results for benzene from Ni(100), shown in Figure 1, showed that benzene desorbed at 475 K, corresponding to an adsorption energy of 119 kJ/mole, and hydrogen evolution from benzene decomposition occurred at 490 K. The TPR results for benzene on Ni(111) showed that benzene desorption occurred at 300 K, corresponding to an adsorption energy of 75 kJ/mole, and benzene decomposition occurred at 460 K. The reflection infrared results showed that no C-H stretches or ring vibrations were infrared active for benzene adsorbed on either nickel surface indicating that adsorption occurred with the ring parallel to the surface on both crystallographic planes.
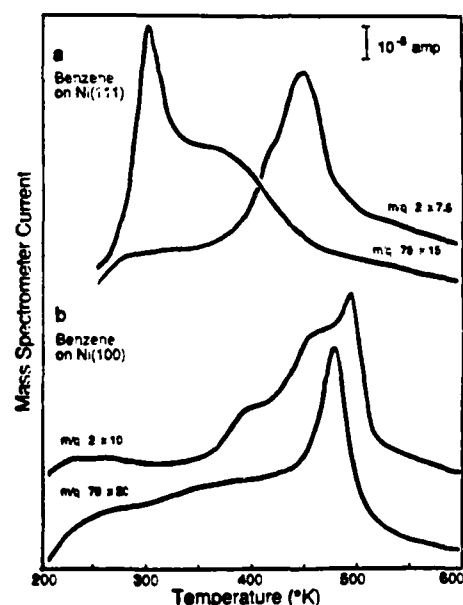

Figure 1. Temperature Programmed Reaction of Benzene on Ni(100) and Ni(111)

The bonding interaction between the benzene and the nickel surface is the result of electron donation from the carbon p-orbitals into unfilled nickel d-orbitals at the surface. The most stable binding configuration for the benzene on the two crystal planes of nickel, as determined by EHT, are shown below, along with the calculated binding energies.
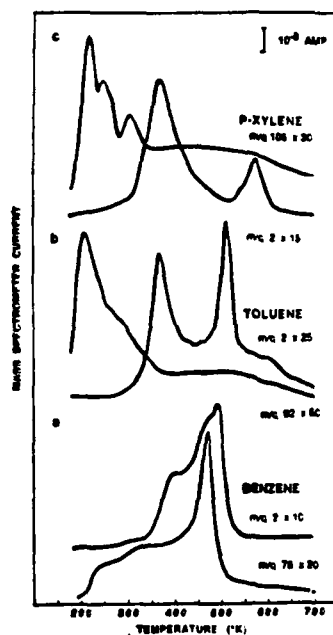
Figure 2. Temperature Programmed Reaction of Methyl Substituted Benzenes on Ni(100)

The extended Hückel calculations show that even with the methyl groups the most stable bonding configurations are with the ring nearly parallel to the surface. Methyl substituents weaken the bonding to the surface primarily by destabilizing the π-bond with the surface due to changes in symmetry of the molecular orbitals; the repulsive interaction of the methyl group was much less significant. Table I summarizes the predicted effects of the methyl groups on the bonding of methyl substituted benzenes on Ni(100). The EH results appear to over estimate the destabilization effect of the methyl groups on the bonding to the surface. There are two corrections that bring the EH results into better agreement with the experiments. First is the allowing the possibility of non-parallel configurations. As the results in Table I indicate the maximum binding energies may occur with the ring slightly tilted relative to the surface. The RAIS results show slight evidence for ring vibrations for o-xylene which is consistent with this observation. The EH calculations also neglect dispersion forces, which become appreciable as the molecular size increases as seen in Table I. The EH calculations also suggest that there are several different adsorption configurations for xylenes with small (10-20 kJ/mole) differences in the binding energies. It may be possible that packing arrangements of the toluene and xylenes may result in the multiple desorption peaks observed with TPR.
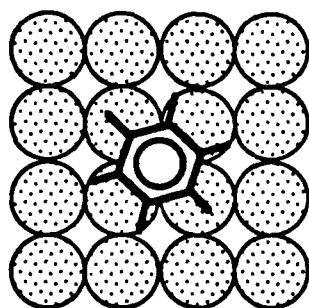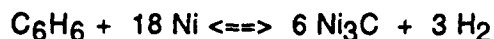
Ni(100)
Ni-ring distance = 2.2 Å
E_{bind} = 129 kJ/mole
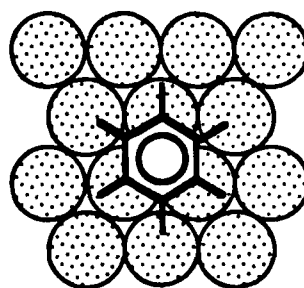
Ni (111)
Ni-ring distance =2.5 Å
E_{bind} = 84 kJ/mole

The EHT calculations agree well with the experimental results and indicate that benzene is more strongly adsorbed on the Ni(100) surface than the Ni(111) surface because of greater carbon-p metal-d overlap.

The decomposition of benzene on nickel surfaces to form dihydrogen and adsorbed carbon was found to be insensitive to the surface structure. The equilibrium for the reaction

$$C_6H_6 + 18\,Ni \Longleftrightarrow 6\,Ni_3C + 3\,H_2$$

only becomes favorable for benzene dissociation at temperatures above 470 K at a dihydrogen pressure of 10^{-8} torr [3]. This indicates that benzene decomposition to yield dihydrogen is thermodynamically limited on both Ni(111) and Ni(100).

Effect of methyl-group substituents on Benzene Adsorption

The adsorption of toluene, o-,m-, and p-xlyene and mesitylene were all examined on Ni(100). As shown in Figure 2 the methyl groups greatly reduced the binding energy of the molecule on the surface. Methyl substituents were found to decrease the the adsorption energy about 65 kJ/mole relative to benzene, independent of the number of substituents. Infrared spectroscopy indicated that the rings were nearly parallel to the surface in all cases as the ring vibrations were weak or non-existent.

Benzene and mesitylene each desorbed in a single peak, indicative of a single adsorbed configuration. In contrast, toluene and the xylenes exhibited several additional lesser peaks or shoulders suggesting the possibility of multiple binding configurations. The placement of the methyi groups also influucenced the reactivity of the moeicule with the surface: m- and p-xylene decomposed to give only H_2 and adsorbed carbon, while o-xylene evolved various hydrocarbon species as well.

Table I

Methyl Substituted Benzenes on Ni(100)

Molecule	Expt.	Binding Energy (kJ/mole) Extended Hückel		Van der Waals
		Flat	Tilted	
Benzene	119	129		25
Toluene	53-75	40	$56(\theta=7^\circ)$	30
O-xylene	53-73	22	$64(\theta=14^\circ)$	34
M-xylene	53-74	26	$58\ (\theta=18^\circ)$	34
P-xylene	53-75	46		34
Mesitylene	53	9		39

The reactivity of o-xylene relative to the m- and p- isomers appears to result from a combination increased electrophilic activity for di-substitution along with a favorable molecular configuration. The enhancement of electrophilic reactivity relative to benzene may be predicted from protodetritiation experiments for methyl substituted benzenes [4]. EHT predicts that m- and o-xylene are tilted relative to the surface. For m-xylene the carbon atoms brought closest to the surface have negligible increased activity for electrophilic substitution. O-xylene has two carbons brought in close contact with the surface that have very enchanceed electrophilic activity. This leads to the formation of an edge bonded moiety that decomposed by C-C bond scisson to form the various hydrocarbon products observed with o-xylene.

Adsorption and Polymerization of Aniline

The activity of the benzene ring for electrophilic substitution is greatly enhanced due to the presence of an amino group. TPR results for aniline demonstrate a dramatic change in the adsorption/reaction behavior of aniline relative to benzene. Aniline is obsereved to adsorb in a multilayer structure below 200 K on Ni(100). The multilayer sublimates at 260 K. Dihydrogen is also found to desorb at 260 K. Experiments with aniline-2,3,4,5,6-d_5 showed that for each aniline that remained adsorbed on the surface two hydrogen atoms were lost, one from the ring and one from the amine group. The partially dehydrogenated aniline decomposed to

yield dihydrogen, HCN and other light gases at 960 K, indicating an exceptionally stable surface species. Infrared results indicate that the multilayer is randomly oriented as the vibrational spectrum is identical to liquid aniline. Upon heating to 450 K, however, the adsorbed aniline species is highly oriented. The absence of any ring vibrations or C-H stretches, coupled with the presence of a strong N-H stretch at 3300 cm^{-1} indicates the adsorbed aniline has the phenyl rings aligned parallel to the surface with an N-H bond oriented perpendicular to the surface.

The thermal stability of the adsorbed species and the reaction stoichiometry are accounted for by the polymerization of aniline to form a highly oriented poly(aniline) film. The binding site configuration for aniline suggested by extended Hückel calculations orients the molecules for attack of the amine group on the para position of a neighboring aniline molecule leading to a linear chain of poly(aniline). The electron density for the adsorbed aniline show the electron density around the nitrogen is decreased and the electron density at the para position is increased relative to the free molecule. This change in electron density results in the amino group being a stronger electrophile when aniline is adsorbed and the para position on the ring becomes more suceptible to electrophilic attack facilitating the oligimerization of aniline.

Adsorption and Reaction of Benzonitrile

Whereas the amino group is known to increase electrophilic reactivity of benzene the cyano group acts as an electron withdrawing group decreasing the electrophilic reactivity of benzene. This analogy is also carried over in the case of surface reactions. TPR results of benzonitrile shown in Figure 3 indicate that benzonitrile forms a multilayer below 180 K, and the multilayer sublimates at 230 K.
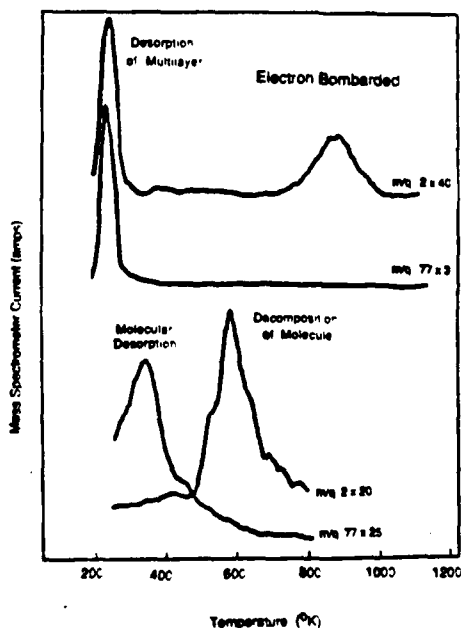

Figure 3. Temperature Programmed Reaction of Benzonitrile on Ni(111)

Reflection infrared results indicate the multilayer is randomly oriented with the presence of both C-N stretchs at 2200n cm^{-1} and ring vibrations at 1460, 1500 and 1610 cm^{-1}. A monolayer of benzonitrile remains adsorbed which desorbs at 360 K. The monolayer is adsorbed with the cyanogroup parallel to the surface and the phenyl ring tilted relative to the surface. The infrared spectra taken at 270 K shows no C-N stretch and shows only two of the ring vibrations. The third ring vibration for the phenyl ring is a ring compression that is parallel to the surface and hence not infrared active when benzonitrile is adsorbed as shown below.
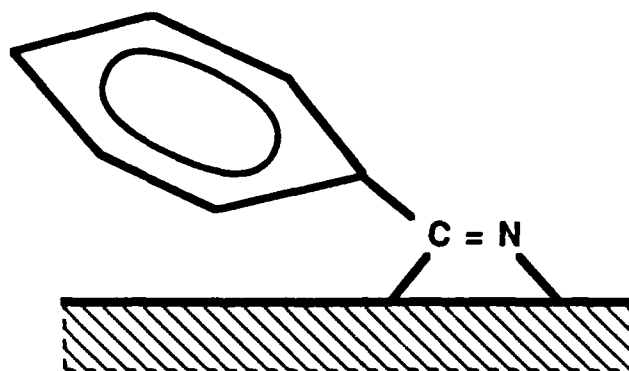
Benzonitrile desorption from the monolayer occurs at 350 K, with a binding energy of 80 kJ/mole. The reduction in binding energy relative to benzene results from the electron withdrawing nature of the cyano group reducing the ability of the phenyl ring to bond with the surface.

Enhancement of Electrophilic Activity at Surfaces

Electrophilic substitution reactions resulting in surface polymerization can be enhanced by increasing the electron density at the surface. This may be done electrochemically by placing a negative potential on the surface. Benzene, aniline, and a variety of aromatic molecules can be polymerized at metal surfaces by anodic deposition [5]. Aniline, thiophene, and lutidene films prepared by electrochemical techniques have been shown to be structurally similar to those films produced catalytically as described above.

A second approach to enhance electrophilic substitution of aromatics to facilitate polymerization is to shoot electrons at the surface. Figure 3 compares the TPR of benzonitrile with and without electron bombardment. The electron bombardment results in a thermally very stable film that decomposes at 900 K to yield a variety of light gases. This film shows the same structural and thermal characteristics that the poly(aniline) displayed. The electron bombardment increased electron density in the aromatic ring to offset the electron withdrawing effect of the cyano group and hence induced polymerization.

It has been shown that nickel surfaces act as electron acceptors interact with aromatic molecules facilitating electrophilic reaction behavior. The conclusions from the effects of substituent groups are summarized below.

Effect of Substituent Groups on Ni(111)

	Benzene	Toluene	Aniline	Benzonitrile
Adsorption Geometry	Ring flat	Ring nearly flat	Ring flat	Ring tilted
Bonding Mode	π-bonding	Destabilized π-bonding	Enhanced π-bonding	σ-bonds via CN group
Reactivity	Decomposition equilibrium limited	Decomposition equilibrium limited	Ring activated to electrophilic reaction: POLYMERIZATION	Decreased reactivity

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2) A.K. Myers and J.B. Benziger, Langmuir, 3 (1987) 414-423.
3) G.R. Schoofs and J.B. Benziger, Langmuir, 4 (1988) 526-532.
4) A. Streitweiser and C.H. Heathcock, Introduction to Organic Chemistry, Macmillan, New York, 1967.
5) J.B. Benziger, N. Franchina, and G.R. Schoofs, in Molecular Phenomena at Electrode Surfaces, M.P. Soriaga, ed., American Chemical Society, Washington D.C., (1988) 83-98.

KINETICS OF CO ADSORPTION/DESORPTION BY DYNAMIC INFRARED SPECTROSCOPY

Dynamic infrared spectroscopy has been used to characterize the adsorption/desorption kinetics of CO on a platinum foil. The CO(ads) stretching band at circa 2050 cm^{-1} was monitored in the presence of a pulsed molecular beam of CO to determine the rates of adsorption and desorption of CO. The rate of carbon buildup from low levels of impurities was also followed from a gradual decline of the adsorptive capacity of the surface.

Adsorption Kinetics

Adsorption kinetics of CO on Pt were measured by following the infrared absorption of the CO stretch at 2070 cm^{-1} as individual pulses of CO were allowed to impinge on the sample. The experimental results are shown in Figure 4 for a sample temperature of 333 K and an exposure of 0.8 L per pulse. These results show an sticking probability, S_0, of approximately 0.4, with the sticking coefficient constant to a coverage of 0.8 saturation coverage and then decreasing. No significant variation in the sticking probability with sample temperature was observed in the temperature range 300-400 K.
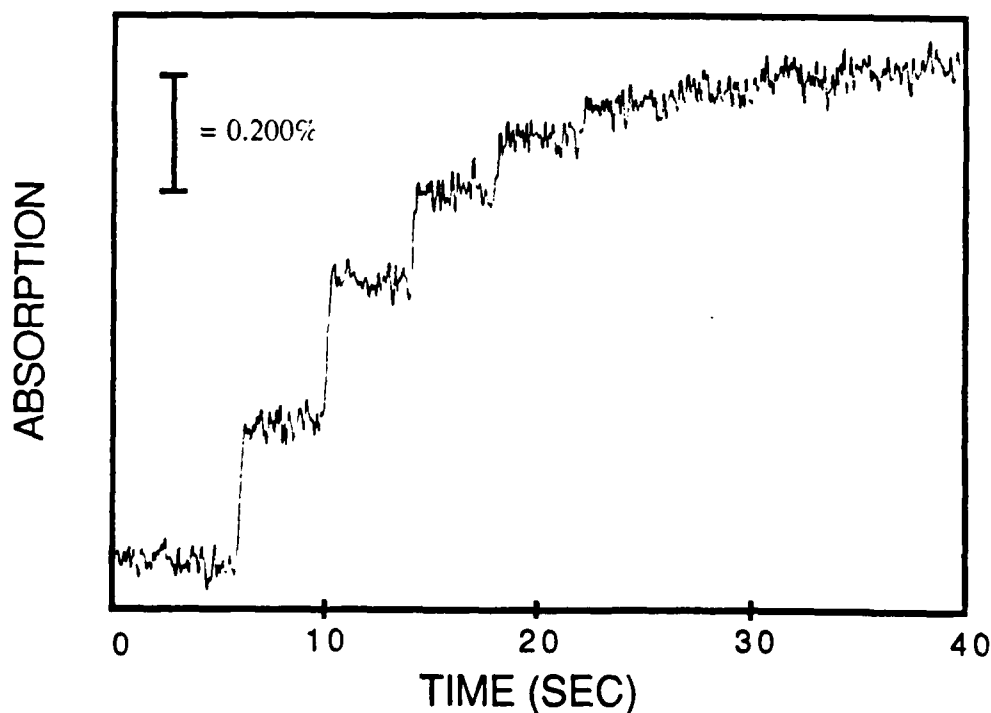

Figure 4. Pulsed CO Ausorption on annealed Pt foil at 333 K. Absorption at 2070 cm^{-1}, flux is 8×10^{14} molecules/cm^2/pulse.

Infrared Absorption Intensity and Surface Coverage

To use the dynamic changes in infrared absorption to determine surface kinetics it was necessary to correlate absorption intensity with surface coverages. Two effects caused the intensity variation to be non-linear with surface coverage. Dipole-dipole coupling at high coverage resulted in a decrease in the dynamic dipole and reduce the effective absorption coefficient. Additionally the absorption frequency shifts to higher wavenumber with increasing coverage so that part of the intensity change with coverage resulted from this peak shift. The frequency shift is illustrated in Figure 5. The spectra shown in Figure 5 show an additional feature of regular spikes superimposed on the spectral trace. These spikes result from taking the spectrum while pulsing the beam, so the spikes correspond to the coverage variation to be examined with the pulsed beam experiment. Different surface coverages are achieved with different beam fluxes.
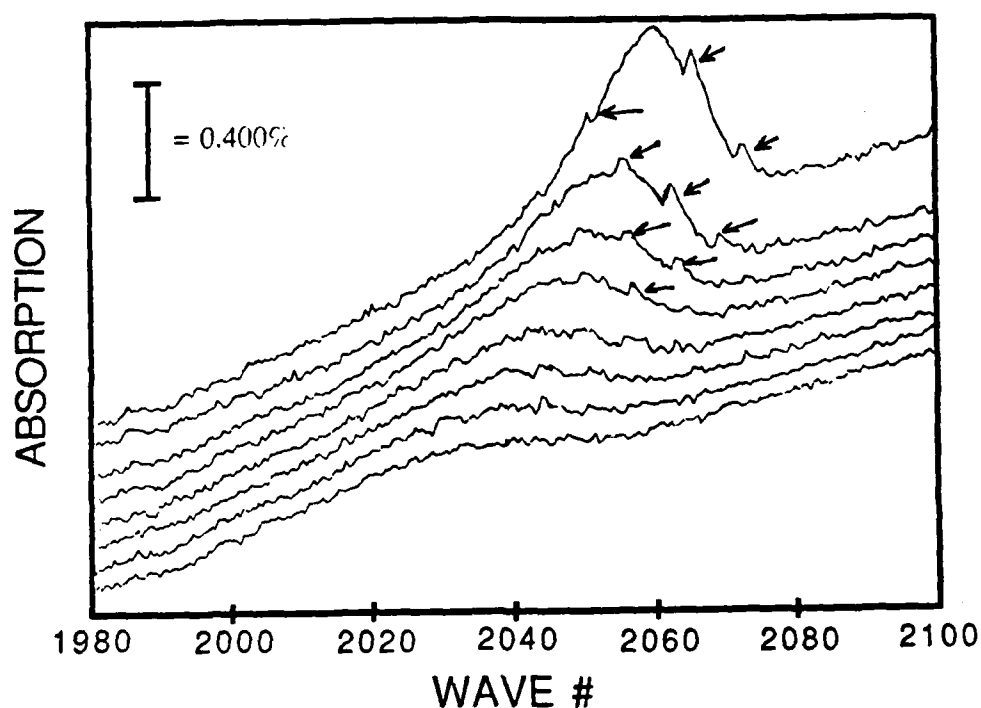

Figure 5. Reflection Infrared Spectra- Coverage variation of CO on a Pt foil.

Dynamic Infrared Kinetics

The kinetics of CO "desorption" were determined from modulated molecular beam spectroscopy. A pulsed beam at 0.25 Hz was allowed to impinge on the surface and the infrared absorption intensity at 2050 cm^{-1} was followed, sample data is shown in Figure 6. Experiments were performed at different pulse fluences and different temperatures. The reaction order was determined from the decay rate in the coverage versus time traces. This was compared with the rate data obtained at different pulse fluences. These two approaches were consistent with first order kinetics. Assuming first order kinetics the rate constants as a function of temperature were determined to find the activation energy of 55 kJ/mol and

pre-exponential factor of 10^6 s^{-1} for the desorption were determined. These values are much lower than found for CO desorption when using the same technique but following the desorbed CO with a mass spectrometer.
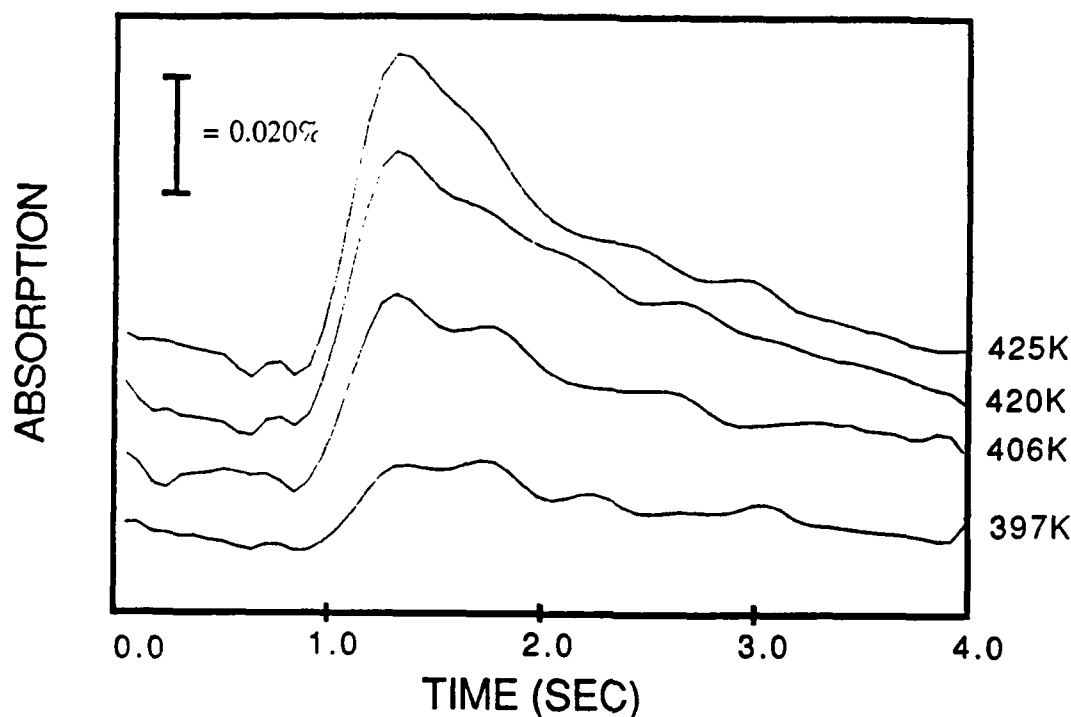

Figure 6. Pulse shapes for Infrared Absorption at 2050 cm^{-1} from CO adsorption on a Pt foil at a fluence of 2.4 x 10^{15} molecules-cm^{-2}-s^{-1}

The low values determined here for the CO "desorption" kinetics appear to result from measuring the kinetics of only one of two steps in the desorption process. The high sticking probability of CO on metals has been ascribed to the existence of a mobile precursor state, in which the CO molecule has two dimensional mobility on the surface. Assuming the desorption process goes through this same precursor state desorption may be viewed as a two step series process.

CO (immobile) ----> CO (mobile) ----> CO (gas)

In the experiment reported here the rate of the first step is being measured, whereas in the experiment where the desorbed CO is followed the overall rate constant is measured. By directly observing the adsorbed state with the infrared spectroscopy it is thus possible to determine the kinetics for individual reaction steps in the desorption process.

Contamination and Reaction Poisoning

A major difficulty with this work has been with delivering molecular beams of adequate purity to avoid poisoning of the surface. It was found that 10-100 ppm of hydrocarbons in the CO resulted in irreversible poison of the surface by a carbon film. This slow poisoning is shown in Figure 7. The sensitivity of surface reactions to the presence of impurities is more sensitive than any analytic technique we have for measuring impurities which has hampered our ability to identify the sources.
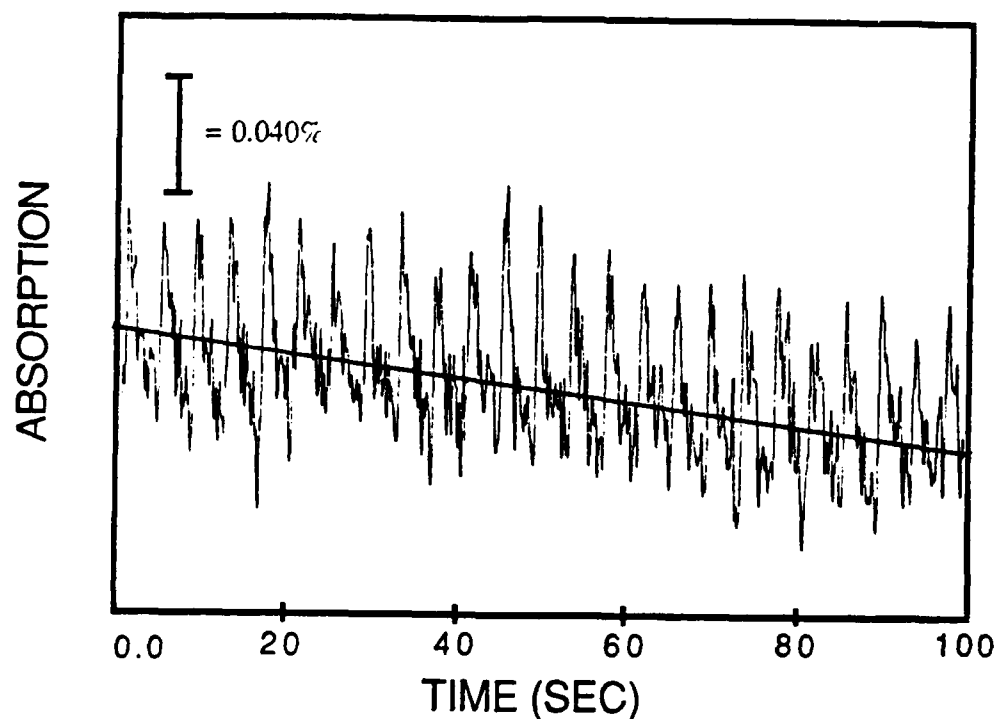

Figure 7. Dynamic infrared spectroscopy of CO on Pt foil showing pulses superimposed on a low term decay of the absorption due to contamination from hydrocarbon impurities.